MINERALOGICAL COMPOSITION OF A SOIL PROFILE FROM THE NAIWA FAMILY OF THE FERRUGINOUS HUMIC LATOSOL GROUP

by

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MINERALOGICAL COMPOSITION OF A SOIL PROFILE FROM THE NAIWA FAMILY OF THE FERRUGINOUS HUMIC LATOSOL GROUP

The development of X-ray diffraction, electron diffraction, and the electron microscope techniques in recent years have greatly facilitated the study of fine grained minerals in soils. Mineralogical content of the colloidal fractions from many soils of the temperate regions has been studied using these techniques; and the results have explained many of the properties exhibited by these soils.

Although many articles have been published on the latosols (formerly called "laterites"), very few studies have been made on the mineralogical content of these soils. Elemental and particle size analyses have been the chief criteria for explaining latosolization; and these criteria have left much confusion and disagreement among workers as to the fundamental processes in latosols. The present investigation was undertaken to characterize the minerals present in a representative latosol by the powder technique of X-ray diffraction and to gain further clarification on the nature of latosols.

The objectives of the investigations reported in this thesis were:

a. To identify the minerals present in the various horizons of a profile from a representative Ferruginous Humic Latosol.

b. To improve the X-ray diffraction method for determination of different minerals occurring in latosols.

c. To determine the weathering stage of this soil, and to extend knowledge of the weathering sequence and its relation to the process of latosolization.

REVIEW OF LITERATURE

The review of literature is divided into two sections. Although the primary objective is the study of the latosols, the general concept of the clay minerals occurring in soils is very important, and a short historical review is presented.

The term laterite, first introduced by Buchanan in 1807 (3), has been the subject of much debate. Presently the term laterite has been abandoned in favor of a more inclusive term "latosol". The soil classification symposium presented in the February 1949 issue of Soil Science suggested a new term for laterite soils (60), as follows:

> "The work planning conference agreed to abandon the term laterite soils, as defined in 'Soils and Man' and to substitute a new term not yet selected. Two terms suggested at the conference are Latosol and Chromosol. This great group of soils includes the more friable and ferruginous of the 'red loams' of European, Asiatic, and Australian literature. It may be synonymous with Marbut's 'Ferruginous Laterite Soils'."

Recent indications are that the term "latosol" has been selected to describe these soils. The terms latosolize (cf. podsolize) and latosolization (cf. podsolization) are the corresponding verb and noun forms adopted herein.

Latosols and latosolization in Hawaii.--The dominant soil forming process in the Hawaiian Islands is latosolization. Cline (4) has classified the latosols of Hawaii into four major groups. They are (a) Low Humic Latosols formed under a rainfall of 15-60 inches per year and under a climatic condition having definitely more dry months alternating with wet months, (b) Humic Latosols which develop under rainfall of approximately 60-150 inches with fewer dry months than wet, (c) Hydrol Humic Latosols occurring in very high rainfall regions of 120-300 inches with no dry months, and (d) Ferruginous Humic Latosols representing the end

stage of weathering for the alternating wet and dry type of climate. The rainfall of the latter soil group ranges from 25-150 inches.

The first extensive work on the elemental analysis of soils from Hawaii according to Hough and Byers (24) was made by Kelley, et al. (36) and later by McGeorge (38). The soils investigated by Hough and Byers have been later identified as latosols according to the classification by Cline (4). The silica/alumina and silica/sesquioxide ratios were calculated for the colloid fraction of these soils, and Hough and Byers (24) concluded these soils were laterite and lateritic soils according to the limits established by Martin and Doyne (42).

Hough et al. (25) studied 21 soil profiles from the Hawaiian Islands and divided the soils into exceedingly young, young, and old, depending on the age of the volcanic ejecta. In the old soils they found that titanium decreased downward while aluminum increased downward. Iron was found to be highest in the horizon next to the top and lowest at the bottom of the profile. Silica was found to be lowest in the layer above the maximum alumina content. On the basis of their study, they concluded that these old soils were "podsolized" from a previously uniform profile. However, the sequence of minerals with depth, indicated by the elemental analysis, follows the depth function of the weathering sequence (32).

Sherman (55) has reported that the latosols of Hawaii fit into several phases of the five stages of soil weathering recognized by Mohr (45). Sherman has concluded from his studies that under alternating wet and dry type of climatic condition, the final end product of weathering is a "lateritic crust" having a high content of iron and titanium minerals. He also reported that under a climate with no definite dry season, an "aluminum oxide laterite", probably bauxite laterite, is formed.

Fujimoto, et al. (12) investigated a very old Ferruginous Humic Latosol and found a high concentration of titanium oxide in the A_2 horizon. They concluded from their studies that the titanium was deposited by solution and not as a result of residual material. Sherman, et al. (57) discussed the soils of the Ferruginous Humic Latosol group. The concentration of heavy minerals in the A_2 horizon make this group of soils unlike other soils described in the literature. Results from elemental analysis of the whole soil and of the colloid fraction revealed that, in the A horizon, Fe_2O_3 and TiO_2 made up the greater portion of the soil constituents; and TiO_2 increased in the A_2 as weathering increased. Sherman has concluded that time plays a very significant role in the formation of the Ferruginous Humic Latosols; i.e. that they are not "equilibrium profiles", thus in accordance with the advancing weathering sequence concept (32).

The mineralogical analysis of the soils in Hawaii has been largely confined thus far to thermal methods. Kelley and Page (37) reported that two soils from Hawaii exhibiting high base exchange capacities possessed strong endothermic peak at 160° C which is characteristic of permutite. They found no X-ray evidence for montmorillonite type of clay minerals and therefore attributed the high base exchange to amorphous material. Dean (7) investigated profiles of soils derived from different parent materials and found kaolinite to be the only type of layer-silicate mineral formed. He also found that soils from Pahoehoe type* lava have high content of kaolinite throughout the profile; whereas soils from Aa type#

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* The Pahoehoe type lava is characterized by a smooth surface and corded forms.

\# The Aa type lava is characterized by rough, angular, jagged blocks.

lava and volcanic ash have more kaolinite in the surface than in the subsoil.

Tanada (58) has presented data from the colloidal fraction of several Hawaiian surface soils. He has found that the SiO_2/Al_2O_3, SiO_2/Fe_2O_3, SiO_2/TiO_2 ratios and kaolinite content decrease with increasing rainfall. His elemental analysis of the soil colloid also showed that the K_2O content is high for some highly weathered soils. Matsusaka and Sherman (43) obtained titration curves for ten important soil groups occurring in Hawaii. Since the buffering capacity is a function of the type and amount of different minerals, the nature of the titration curves serves as a guide to the minerals present. The Ferruginous Humic and Low Humic Latosols were shown to have very little buffering capacities; while the Humic and Hydrol Humic Latosols had pronounced buffering capacities due in part to organic matter content. The lack of buffering capacity of the Ferruginous Humic Latosols was explained on the basis of the decomposition and disappearance of kaolinite and accumulation of free oxides.

Many definitions have been proposed to define a laterite. Fermor (11) suggested in 1911 to limit the term laterites to soils containing over 90 per cent of the oxides of iron, aluminum, titanium, and manganese. Martin and Doyne (42) used the silica/alumina ratio of the clay fraction to be the basis of defining laterites and lateritic soils. Soils having a silica/alumina ratio of less than 1.3 were to be considered laterites, while lateritic soils were limited to 1.3 to 2.0. However, Pendleton (49) has criticized this definition of laterites as he found many profiles to contain more iron than aluminum.

Pendleton and Sharasuvanna (49) state that, "by 'laterite' is meant the material originally described by Buchanan and later more fully by Old-

ham, namely, an illuvial horizon, largely of iron oxides, with slaglike cellular or pisolitic structure, and of such a degree of hardness that it may be quarried out and used for building construction". du Preez (8) has modified this definition and writes, "Laterite is a vesicular, concretionary, cellular, vermicular, slaglike, pisolitic or concrete-like mass consisting chiefly of ferric iron oxides with or without mechanically entangled quarts and minor quantities of alumina and manganese; it is of varying hardness but it is usually shattered when struck a sharp blow with a hammer".

The laterite crust of Hawaii conforms to the definition of du Preez as given above; particularly because hardness is not a requirement for laterites. Sherman (56) has described and hypothesized the genesis of the crust in Hawaii. He considers that lateral movement of water through the friable layer and alternating wet and dry season to be the two main factors involved in its formation. He believes that the water which contains dissolved ions rise to the surface especially at level areas of the slope during the dry season. Mohr (45) and Pendleton (49) consider the crust to be formed by illuviation and consequent erosion rather than upward movement as postulated by Harrassowitz (18) and Sherman (56).

Clay mineral concept.--The crystalline nature of soil clays was suspected by early investigators before the application of X-ray diffraction. Bradfield (2) in 1923 found conclusive evidence that the natural colloid was not a mixture of colloidal SiO_2, Al_2O_3, and Fe_2O_3. Marshall (40) in 1926 conducted experiments on some Rothamsted soil and found much crystalline material to be present. In 1927 Ross (51) asserted that:

> "Most of the clay-forming materials of shales and soils are definitely crystalline minerals with definite chemical and physical properties, although they may be somewhat modified in chemical composition by adsorption and base exchange."

Ross also found that the dominant soil and clay-forming mineral is beidellite rather than kaolinite as previously supposed.

Previous to the work of Hendricks and Fry (22) and Kelley et al. (35), X-ray diffraction technique was applied mainly to clay deposits other than soils. The work of these investigators (22)(35) showed conclusively that soils contain appreciable quantities of crystalline minerals; mainly kaolinite, montmorillonite, and Ordovician bentonite.

The United States Geologic Survey has intensively studied the naturally occurring clays. Ross and Kerr (53) in 1931 reported that the kaolin family* were composed of at least three mineral species: kaolinite, dickite, and nacrite. In 1934, they reported that halloysite also belonged to the kaolin family*, and that allophane was amorphous (54).

From the layer lattice structures proposed by Pauling in 1930 (47)(48), Gruner suggested structures for kaolinite, dickite, and nacrite (15)(16)(17). Mehmel (44) proposed the structure of halloysite and metahalloysite, and he differentiated them not only in axial length but in symmetry of successive plates. Montmorillonite has long been noted for its swelling capacity, and Hoffman, et al. (23) obtained structural configuration through X-ray diffraction patterns that accounted for this swelling. After intensive studies, the United States Geologic Survey published an excellent report on the minerals of the montmorillonite series in 1945 (52).

The importance of isomorphous substitution came to be realized with increasing information on the various clay minerals. They 2:1 layer silicates differ from one another by the degree and kind of replacement

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* The kaolin family is employed herein instead of kaolin group in accord with the classification of Jackson, et al. (31).

occurring in the silica tetrahedron and the alumina octohedron. Aluminum may substitute for silicon in the tetrahedral position as in the micas and illites. Substitution of magnesium and ferrous or ferric iron for aluminum in the octohedral position gives rise to further differentiation. Studies were made by Jackson and Hellman (29), Hellman, et al. (20), and White and Jackson (62) on differentiating montmorillonite from hydrous clay intermediates using different inorganic and organic cations to increase the intensity of the basal diffraction of montmorillonites.

Although the 1:1 layer silicate family has been reported to have isomorphous substitution, Hendricks (21) has given reasons for non-occurrence of partial substitution. The minerals resulting from rather complete isomorphous substitution of these sheets are excellently presented in the publication by Jackson, et al. (31). The knowledge of these substitutions made it possible to explain slight differences in diffraction patterns. Stacking of the plates in slightly different positions (15)(16)(17) gives rise to different clay minerals although identical chemical formulas are obtained. Thus kaolinite, dickite, and nacrite have the same formula and lattice plates but differ in stacking arrangement.

The application of electron microscope has also aided in the identification of clays. Eitel and co-workers (9)(10) and Humbert and Shaw (26)(27) have characterized shapes of kaolinite, montmorillonite, dickite, nontronite, hectorite, illite, and beidellite. Jackson, et al. (30) have suggested uses of electron microscope to study shapes, dispersion, flocculation, aggregation, and mineral weathering.

On the basis of the occurrence of different minerals in variously weathered soils, Jackson, et al. (32) proposed a weathering sequence of

fine-grained minerals. The sequence concept views soils as continuously advancing through the weathering sequence rather than each soil group being in equilibrium with its existing environment. Thus podsolization and latosolization are considered as continuous functions, a concept supported in part by the decrease in quarts content with increasing weathering stage, i.e. approaching latosol stage. The continuity of weathering as proposed by the weathering sequence principle allows for sensitive soil changes in response to changes in the intensity fasters of temperature, water, protons (H^+ ions), and electrons (oxidation and reduction).

The review presented is by no means complete, for the literature on clay minerals today is extensive. However, excellent discussions of clay minerals and their importance in soils have been published, and the reader is referred to them for a complete discussion (14)(41)(46). It should be emphasized that studies of clay minerals were not limited to a few investigators. Marshall (41) writes, "No single person, no one laboratory, carried through all of them. The work was piece meal, individualistic, governed in the 1920's by a wide variety of objectives, and intermingled with much that was later seen to be irrelevent.".

DESCRIPTION OF THE SOIL PROFILE SAMPLED

The description of the Naiwa family of the Ferruginous Humic Latosol was furnished by Dr. G. D. Sherman, The University of Hawaii Agricultural Experiment Station, Honolulu, Territory of Hawaii.

The site of sampling of this profile is 1.5 miles northwest of Waihee point on the Island of Maui. The vegetation zone according to the classification of Ripperton and Hosaka is G_1 (50). The vegetation is composed of stunted guava trees, few koa trees, and bunch grass.

The profile description of the Naiwa family of the Ferruginous Humic Latosol group used in this investigation is given in Table 1.

Table 1. Description of the sampled profile from the Naiwa family of the Ferruginous Humic Latosol group.

Horizon and depth, cm	pH	Structure, color, and class	Remarks
A_1 0 - 20	6.4	A reddish-purple massive silty clay loam having a crumb to granular structure.	High apparent specific gravity.
A_2 20 - 35	6.4	Silty clay loam very similar to A_1. When moist it is massive, when dry it is granular.	When wet distinct contrast between A_1 and A_2 in structure. Little evidence of organic matter.
A-B 35 - 50	6.2	Reddish-brown to reddish-purple clay layer.	Texture of silt loam and is fairly friable. Normal volume weight.
B 50 - 100	6.1	Light reddish-brown very friable clay. Vesicular type of blocky structure when dry, which crumbles with ease.	Has gritty feel of sand when rubbed between the fingers. Normal volume weight.
C 100+	5.4	Reddish-brown silty clay loam which is not as friable as the B horizon.	Contains fragments of latite*. Typical picture of residual weathering.
D Parent rock	3.9	Whitish rotten latite rock. Crushes easily into powder in one's hands.	This rock is impervious to water, and thus promotes the lateral movement of water.

* Latite is a fine-grained igneous rock containing more plagioclase than potash feldspars.

EXPERIMENTAL PROCEDURES

The experimental procedures employed in this investigation consisted of size segregation, X-ray and elemental analyses, and electron microscope examination. Segregation was effected by sieving, gravity sedimentation, and centrifugation. The respective size fractions were X-rayed using appropriate techniques for powder patterns and layer-silicate orientation methods. The particle-size fractions were chemically analyzed for iron, titanium, and potassium. Several samples were analyzed for silica and aluminum. Electron microscope observations were also made of crystal size and degree of dispersion.

Fractionation of the soil sample.—Twenty-five gms of air-dried soil were weighed, and 1:4 nitric acid was added to give a pH of 4. The organic matter was destroyed by adding increments of 30 per cent H_2O_2 until all reaction ceased. The decomposition was undertaken on a hot plate at a temperature of approximately 65° C. After the organic matter was removed, the soil was washed free of salts by centrifuging.

The soil was then transferred to a Waring blender and dispersed with NaOH at pH 9.5. Subsequent to the work employing this method of dispersion, Jackson et al. (33) published a procedure in which boiling in a 2 per cent Na_2CO_3 solution gave better dispersion. (Several samples were viewed with the electron microscope to study the degree of dispersion by means of this improved method of dispersion.) The soil was then passed through a 300-mesh screen, and the passage of the particles was aided with a fine stream of distilled water and a rubber policeman. The particles greater than 50 microns/in diameter remained on the sieve; they were dried, weighed and saved.

The suspension was separated at 20 and 5 microns by sedimentation.

This was accomplished by allowing the suspension to stand quietly for a specified time depending on the particle size and temperature of the suspension. The time of each cutting was determined applying Stoke's law. Tanner and Jackson (59) have published nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration; and these may be consulted for determining appropriate time for each cutting. The fractionation of the coarse and medium silt particles was accomplished by repeated sedimentation and decantation. The fractions were washed, dried, weighed, and saved.

The fine silt was separated from the clay by centrifuging at 500 rpm for approximately 5 minutes using the No. 1 International centrifuge. This was repeated several times for complete segregation. An efficacious method is described in "Soil Analysis--Chemical and Physicochemical Methods" (28). The method consists of allowing the fine silt and clay fractions to stand quietly overnight, then decanting or siphoning off the suspension containing the clay fractions. The latter method eliminates working with a large volume and greatly facilitates the segregation. The fine silt fraction was dried, weighed and saved. It is recommended that this fraction be kept in suspension in order to prevent irreversible dehydration of layer-silicates which might be present (28). If the sample is preserved in this manner, an aliquot is dried and weighed; and the weight of the fraction calculated.

The fraction less than 2 micron/in diameter was separated into two fractions of 2-0.2 microns and less than 0.2 microns by centrifuging with the No. 2 International centrifuge at 2400 rpm for approximately 30 minutes. The centrifugation was repeated until the supernatant liquid appeared clear. This required five centrifugings following the first decantation of the

original suspension. The 2-0.2 micron fraction was brought to volume, an aliquot was taken, dried, and weighed. The sample was saved in suspension in a well-stoppered bottle.

The less than 0.2 micron fraction flocculated upon standing. The clear supernatant liquid was siphoned away, the clay brought to volume, and an aliquot removed, dried, and weighed. The combined medium and fine clay fraction was saved in a stoppered bottle. In case the clay remained in suspension, the clay was flocculated with HCl, the supernatant liquid removed, and the clay re-dispersed. The procedure employed for the size segregation was long and tedious. For a much faster and efficient method the reader is referred to "Soil Analysis--Chemical and Physicochemical Methods" (28).

Preparation of samples for X-ray diffraction analysis.--An aliquot representing a 50 mgm sample (or a weighed portion of the coarser fractions) was removed and placed in 100 ml tubes described by Truog, et al. (61). In the powder technique, the samples were not glycerol solvated because the absence of 2:1 layer lattice silicates was assumed. Later work employing the layer-silicate orientation technique gave indication of presence of montmorillonite, and the samples were thereafter glycerol solvated.

The samples were calcium-saturated following the procedure described by Jackson and Hellman (29). The 50 mgm aliquots in the centrifuge tubes were flocculated with pH 3.5 HCl solution. The flocculs were separated by centrifuging. Each sample was transferred to a beaker and approximately 60 ml of 0.5 N NaAc having a pH of 3.5 adjusted with HCl was added. The samples were boiled for five minutes; at the end of this time three ml of 10 N $CaCl_2$ were added to give a 0.5 N $CaCl_2$ solution. The suspensions

were then centrifuged, and the supernatant liquid decanted. In order to assure complete calcium-saturation, the samples were washed three times with 0.5 N $CaCl_2$ (pH 7.0 with $Ca(OH)_2$), three times with 1.0 N $Ca(Ac)_2$, and three more times with 0.5 N $CaCl_2$ (pH 7.0 with $Ca(OH)_2$). To remove the excess $CaCl_2$, the samples were washed once with CO_2-free water, once with 70 per cent methyl alcohol, twice with 90 per cent methyl alcohol, and finally with absolute methanol until completely free of chlorides. The complete removal of the chlorides was ascertained by testing a portion of the decanted supernatant liquid with silver nitrate solution. The samples were washed with benzene and allowed to dry on a watch glass in a current of dry air. After drying they were carefully scraped from the glass and placed in a tightly stoppered vial.

Total elemental analysis of size fractions.--The procedure for total elemental analysis applied in this study was developed and described in detail by Corey (6). Total iron and titanium were determined colorimetrically by complexing with tiron. After reading the iron at 540 millimicrons, the iron was reduced with sodium dithionite, and the titanium read at 400 millimicrons. Potassium was determined emission-spectrophotometrically.

Silica and aluminum were also determined colorimetrically. Silica formed a complex with ammonium molybdate, and its concentration read at 400 millimicrons. Aluminum was complexed with aluminon reagent and read at 520 millimicrons.

X-ray diffraction procedure.--The samples were mounted on a 90° sector wedge. Clays high in iron and aluminum oxides showed a strong tendency to form a "cake" upon drying. When this occurred, the samples were gently ground in an agate mortar and then mounted on the wedge.

The powder patterns were obtained using a circular camera employing Kodak no screen medical X-ray film. Manganese dioxide in cellulose acetate film filter placed in contact with the photographic film was used on several samples. When filters were used to remove diffraction by Fe K_β radiations, a strip covering one-half of the film was placed between the camera circumference and the X-ray film. The X-rays were generated from an iron target by applying 48 kv and 8 ma. The films were exposed for 1.5 hours.

The films were developed for 8 minutes in Kodak X-ray developer, washed for one minute in water, and fixed in general X-ray fixer for 20 minutes; all of the solutions were first brought to a temperature of 20° C in a water bath. After fixing, the films were washed for 30 minutes in a pan having a constant supply of fresh water. The films were then dried and saved.

With the layer-silicate orientation method, the soils were sodium-saturated in water solution, and glycerol solvated using 0.02 ml of glycerol for the 50 mgm of sample. The soils were placed on microscope slides with a medicine dropper, and slowly allowed to dry. The General Electric XRD-3 apparatus was used, equipped with a Leeds and Northrup recorder. The X-rays were generated from a copper target at 50 kv and 16 ma; nickel filters were used to remove Cu K_β radiations. The beam slits of 1° and 0.1°, time constant of 6 seconds, and scale reading "2" for sensitivity and balance were used. The copper radiation was not very satisfactory for the high-iron samples.

Identification of minerals occurring in latosols.--Obviously, before percentage allocations can be made, lines specific for each mineral must be chosen. These lines should not only be characteristic of the

mineral, but must be of sufficient intensity to be detectable in low concentrations. The characteristic spacings of the major minerals identified are listed in Table 2.

Hematite (Fe_2O_3) is easily distinguished when present by the 2.69, 2.51, and 1.69 A lines. Goethite (FeOOH) is distinguished from hematite by the 2.45 and 4.18 A lines. Both minerals possess the 2.69 A line; consequently this line cannot be used for their differentiation. In the presence of quartz (SiO_2), the 4.18 A line of goethite may be partly obscured by the 4.29 A line of quartz. The overlap of the two diffraction lines become very marked in the smaller size fractions as diffraction lines become diffuse with decreasing particle size. Although gibbsite, $Al(OH)_3$, has 2.48 and 2.40 A lines, these lines appear as two distinct lines. When goethite is present, the three lines of 2.40, 2.45, and 2.48 A appear as a broad band. It was also found that hematite and gibbsite show an inverse relationship, therefore identification was simplified in most cases. The 2.51 A line was chosen for hematite identification, and the 4.18 A line in conjunction with the 2.45 A line for goethite identification.

Identification of gibbsite in the presence of layer silicates may cause difficulty. Layer silicates possess a 4.45 A line with the K_α for which the K_β diffraction line from the iron X-rays falls close to the position of the 4.80 A K_α line of gibbsite. Gibbsite also has a 4.41 A line. This difficulty can be remedied by using a filter which removes the K_β radiation. Manganese is specific for iron K_β radiations, and therefore a manganese dioxide filter was employed. (See figure 7e and note slight decrease in intensity of the 4.80 A line indicating gibbsite.)

In addition to the diffraction spacings, magnetite ($FeO \cdot Fe_2O_3$) was easily identified by the spotted character of the lines especially in the

Table 2. Principal lines of the major minerals identified in the Naiwa family of the Ferruginous Humic Latosol group. The values are d/n angstrom spacings in decreasing order.

Illite	Hydrous Clay Intermediates	Kaolinite	Gibbsite	Magnetite	Goethite	Hematite	Anatase
10.0	10.0-14.5						
		7.2					
4.9			4.8				
					4.6		
4.4	4.4	4.4	4.2		4.18		
		3.8				3.67	
		3.57					3.51
3.33		3.38	3.31				
			3.12				
			3.07				
2.98				2.98			
			2.81				
				2.79			
					2.69	2.69	
2.56		2.50		2.54		2.51	
			2.42	2.43	2.45		
		2.33	2.38				2.37
2.24		2.29	2.27				
			2.22		2.18	2.20	
			2.15	2.09			
			2.03				
1.99		1.99	1.98				
			1.90				1.89
						1.83	
			1.79		1.80		
			1.73	1.71	1.72		
						1.69	1.69
1.64		1.66	1.67				1.66
		1.62		1.61			
					1.56	1.59	
1.50					1.51		
		1.49		1.48	1.47	1.48	
			1.45		1.45	1.45	1.45

coarser fractions. Anatase (TiO_2) was characterised by the 3.51 A line. This was the only line present for anatase; and since the other positively identified minerals did not possess this line, it was attributed to anatase. The 3.51 A line is marked "An" in figure 7b.

The identification of hydrous clay intermediates was accomplished through the use of the XRD-3 apparatus. Studies on the powder patterns revealed very little evidence of its presence; however when the samples were studied by the layer-silicate orientation technique, a diffraction pattern was obtained showing the "OOL" spacing of the hydrous clay intermediates ranging from 10 to 14 A (Figure 12). Potassium analysis further substantiated this conclusion. Although the fraction containing the highest content of hydrous clay intermediates was insufficient to run elemental analysis, sufficient data were obtained to estimate the content of potassium for this sample. Figures 5 and 6 are electron micrographs of the clay fraction from the horizon giving X-ray patterns for hydrous clay intermediates.

Kaolinite was identified by the 7.2 A line. The feldspars are characterised by the 3.25 and 3.20 A line for orthoclase and albite, respectively. Only one line was generally noted on the film patterns. No other line could be found; nevertheless this does not invalidate the feldspars since the lines other than the principal line is very weak according to the Hanawalt tables and standard feldspar diffraction patterns obtained in this laboratory.

The d/n spacings of the principal minerals identified in this investigation has been tabulated and presented in Table 2. Hydrous clay intermediates are not yet well identified and only the two principal lines are given.

Mineral allocation procedure.--Kelley and Page (37), Jeffries and Jackson (34), and many others have emphasized that X-ray diffraction alone is not sufficient for complete mineralogical analysis. In this investigation, the allocation of minerals was accomplished in the following manner. The diffraction spacing was calculated by measuring the distance from the center of the undiffracted beam to the line and calculating the d/n spacing by Bragg's law. The diffraction spacings were then compared with the values given in the card file of the American Society for Testing Material and the National Research Council. Further verification was obtained from standard mineral patterns of this laboratory.

The percentage allocation was based on the intensity of the diffraction lines and from the results obtained from the elemental analysis. Analysis of TiO_2 was reported as anatase although only a few samples gave anatase lines in the patterns. It is probable that considerable TiO_2 is present in some hydrated form such as leucoxene, $TiO_2 \cdot nH_2O$, especially in the finer sized fractions, and to some extent as ilmenite, $FeO \cdot TiO_2$.

Iron oxide content was allocated to hematite, goethite, and magnetite. Where ever magnetite occurred, no other free oxide was present; therefore all iron present in these fractions were reported as magnetite. Although hematite was the dominant iron mineral, several samples gave goethite as well as hematite. The iron was allocated using samples containing only hematite as standard and the difference between the hematite and total Fe_2O_3 was considered to be goethite.

Due to the high content of amorphous silicate, the difficulty of allocation was increased. The existence of amorphous silicate was concluded from the X-ray patterns and elemental analysis. This was especially evident in the fine silt fractions. Elemental analysis showed over

20 per cent silica; but X-ray diffraction lines for layer silicate and quartz were very weak. Quartz lines are distinct even as low as 10 per cent, and therefore all the silica could not be attributed to quartz. Aluminum showed the same behavior. After allocating aluminum to gibbsite and to layer silicates from standard mineral patterns, the remainder was placed in the amorphous silicate fraction. The percentage of amorphous silicate was determined by subtracting the sum of the known minerals from 100 per cent. The high content of these amorphous material in the profile is significant and was established in a valid manner.

PARTICLE SIZE-DISTRIBUTION AND ELEMENTAL ANALYSIS

Results of the size-distribution and elemental analysis are presented in this section. The importance of complete dispersion for mechanical analysis and the data on elemental analysis were found to be essential for the characterization of these latosol colloids.

Size-distribution of soil fractions.--Particle size-distribution is an integral part in the study of soil; therefore the results of such analysis are reported in Table 3.

The low content of medium and fine clay fractions in the A horizons suggests eluviation, and the high content of clay in the B horizon suggests illuviation. The A_1 horizon has a high concentration of particles in the medium silt fraction, and in the A_2 horizon 20 per cent of the sample is concentrated in the coarse silt fraction. These high concentrations of particles in the two horizons led to studies on dispersion.

Several fractions viewed with the electron microscope indicated that the NaOH dispersion treatment was inadequate. The 5-2 and 2-0.2 micron fractions contained aggregates, and the electron micrographs from these fractions are shown in figures 1 and 2. Redispersion of several samples gave an average value of 25 per cent of the sample being below the lower size limits for the 20-5 and 5-2 micron fractions and 8 per cent for the 2-0.2 micron fraction. Figures 3 and 4 show the samples after the sodium carbonate treatment. These results are similar to those reported for soils of temperate regions in the original publication of the 2 per cent Na_2CO_3 method (33).

Lack of complete dispersion has affected the results for the mechanical analysis (Table 3) somewhat, but it does not greatly alter the mineral

Table 3 The percentage of sand, silt and clay in the different horizons of a Ferruginous Humic Latosol (Naiwa family) profile from West Maui*

Size separate	Percentage of separate in horizon					
	47-248 A1	47-249 A2	47-250 A-B	47-251 B	47-252 C	47-253 D
Greater than 50 microns	2.69	2.85	1.59	1.27	2.10	9.47
50-20 microns	10.81	21.65	4.27	4.57	8.25	14.39
20-5 microns	24.32	12.19	10.10	13.67	20.26	28.18
5-2 microns	20.03	25.50	13.70	11.11	20.75	12.54
2-0.2 microns	23.27	27.44	34.72	30.00	19.12	10.80
Smaller than 0.2 microns	9.73	7.90	23.20	23.34	14.38	7.04
	Total percentage of main separates					
Sand	2.69	2.85	1.59	1.27	2.10	9.47
Silt	55.16	59.34	28.07	29.35	49.26	55.11
Clay	33.00	34.34	57.92	53.34	33.50	17.84
Total#	90.85	96.53	87.58	83.96	84.86	82.42

* Data from Dr. G. D. Sherman, The University of Hawaii Agricultural Experiment Station except 47-253 which was segregated at the University of Wisconsin.

\# Failure to total to 100 per cent is due to loss of weight of organic matter and probably some hydroxyl from gibbsite in the 105° C oven.

identification as a function of particle size. Identification of large crystals of hematite was based on the spotted character of the X-ray diffraction patterns. The kaolinite in the large sizes from the C and D horizons was identified with the petrographic microscope. The particles under investigation showed the characteristic hexagonal shape of kaolinite. Thus the particle size-distribution of the minerals is not invalidated; only slightly different results would be expected if the dispersion had been more complete.

The results however do emphasize the necessity of a dispersion which is adequate. Boiling in 2 per cent sodium carbonate (33) is a much more effective dispersion treatment than the older methods, and this procedure is recommended.

The A-B and B horizons contain sufficient clay-size particles to be of "clay" textural class according to the classification of the United States Bureau of Plant Industry, Soils and Agricultural Engineering; although field observations of the soil consistency suggested silt and sand texture. The discrepancy arises from the lack of plastic minerals in the latosols.

The more highly weathered condition of the C horizon as compared to the partially decomposed rock (D horizon) is reflected in the higher clay content and lower silt and sand fractions. However the intensive weathering conditions operating on this profile are evident by the 17.8 per cent combined clay fractions in the D horizon (Table 3).

The total percentage of the main separates deviates highly from 100 per cent. This is probably caused by the high content of gibbsite in the A-B, B, C, and D horizons. Gibbsite is known to lose water at slightly over 100° C. Since the samples were dried in a 105° C oven until all water was removed, the mineral percentage based on the air dry weight of

the soil is lower. Recalculation was not done because the allocation of gibbsite is not of sufficient accuracy.

Figure 1.—Aggregates from the 5-2 micron fraction after NaOH dispersion treatment.

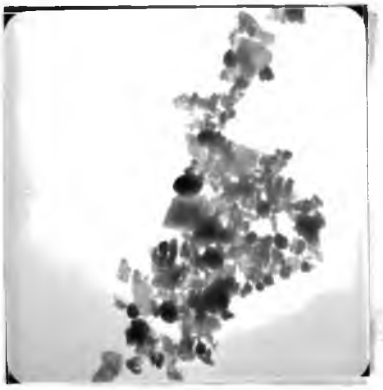

Figure 2.—Coarse clay aggregates. The individual particles are within the 2-0.2 micron size limit.

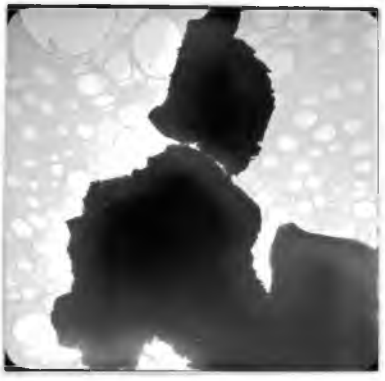

Figure 3.—Particles of the 5-2 micron fraction after dispersion with 2% boiling Na_2CO_3. Note sharp edges.

Figure 4.—Representative crystal from the 5-2 micron fraction. Sharp edges suggest growth rather than "weathering away" of the crystal.

Elemental analysis of size fractions.—Elemental analysis serves as a valuable aid in the study of the chemistry of soil formation and also as an important guide in substantiating mineralogical identification and estimation. The results of elemental analyses obtained on the fractions are summarized in Table 4. Potassium is reported as K, iron as Fe_2O_3, aluminum as $Al(OH)_3$, titanium as TiO_2, and silicon as SiO_2. In samples in which the total elemental analysis is greater than 100 per cent, the chief cause for this discrepancy is the degree of hydroxylation of aluminum. Aluminum hydroxide has a chemical factor 1.53 times greater than Al_2O_3. The latter is the form in which it exists in silicates.

In the A_1 and A_2 horizons, iron decreases with decreasing size. The A-B transition zone shows the same trend except in the coarse clay fraction in which the Fe_2O_3 is higher than the medium and fine silt. The B horizon contains the highest iron in the coarse clay fraction (48.0%) followed by the coarse silt fraction (47.2%). The highest content of iron in the C horizon is in the coarse silt fraction with the medium and fine silt being low. The clay fractions have approximately 22 per cent iron oxides. The partially decomposed parent rock analyzed 16.0 and 11.5 per cent iron oxide in the coarse and medium silt respectively; the fine silt, coarse clay, and medium and fine clay each contained about 5 per cent iron oxide.

The highest content of iron oxide analyzed is in the coarse silt fraction of the A_2 horizon. In the silt fractions, iron oxide was highest in the A_2 horizon in every case. The clay fractions showed highest iron oxide in the B horizon.

Titanium shows an interesting behavior. In every case its concentration is directly proportional to the concentration of iron. Wherever iron is high, titanium is also high; and decrease in iron was accompanied

Table 4. Elemental analysis of the silt and clay fractions from the Naiwa family of the Ferruginous Humic Latosol group.

Horizon	Depth of profile, cm	Percentage constituents of oven dry mineral fractions					
		K	Fe_2O_3	TiO_2	$Al(OH)_3$	SiO_2	Total
		Coarse silt, 50 to 20 microns					
A_1	0-20	0.39	59.0	14.4	3.76		
A_2	20-35	0.11	74.1	16.7	3.61		
A-B	35-50	0.10	65.5	13.0	16.2		
B	50-100	0.19	47.2	8.10	20.6		
C	100+	0.02	31.9	6.18			
D	Partially dec. rock	0.06	16.0	2.79			
		Medium silt, 20 to 5 microns					
A_1	0-20	0.76	45.8	7.45			
A_2	20-35	0.22	60.1	9.55	8.30	22.5	97.5
A-B	35-50	0.17	43.3	7.10			
B	50-100	0.15	35.2	6.35			
C	100+	0.00	9.53	1.05	78.0	20.6	109.2
D	Partially dec. rock	0.02	11.5	1.47	66.6	29.0	108.6
		Fine silt, 5 to 2 microns					
A_1	0-20	0.82	39.3	6.01	21.7		
A_2	20-35	0.51	52.3	9.02	19.4		
A-B	35-50	0.45	36.5	5.21	49.1	23.2	114.0
B	50-100	0.27	28.6	3.68	50.5	23.5	106.3
C	100+	0.04	8.08	1.25	81.7	20.7	111.7
D	Partially dec. rock	0.04	4.58	0.84	74.7	26.1	106.2
		Coarse clay, 2 to 0.2 microns					
A_1	0-20	1.4	31.8	4.01	24.2		
A_2	20-35	1.6	44.8	5.85	25.5		
A-B	35-50	1.2	45.4	5.56	24.1		
B	50-100	0.77	48.0	5.51	22.9		
C	100+	0.22	22.9	2.92	60.0	12.9	108.7
D	Partially dec. rock	0.10	4.94	0.97	59.2		
		Medium and fine clay, less than 0.2 microns					
A_1	0-20	*	*	*			
A_2	20-35	1.4	26.2	3.34	34.7	21.5	85.7
A-B	35-50	0.96	29.2	3.81	36.4	20.7	89.1
B	50-100	0.77	34.0	2.95	60.7		
C	100+	0.25	22.7	2.50	70.0	12.5	107.7
D	Partially dec. rock	0.13	5.62	1.00	75.2		

* Insufficient sample for elemental analysis.

by a lower titanium content. This would imply that the titanium is present as a compound of iron such as ilmenite, $TiO_2 \cdot FeO$. It could also result from the adjacent position of the hematite and anatase weathering stages (12 and 13, respectively). There is a high concentration of titanium in the medium and fine clay fractions which suggests probable chemical weathering of the titanium mineral. The highest titanium content is in the coarse silt fraction of the A_2 horizon, which also has the highest iron oxide content.

Potassium is used as a criterion for estimating illite and 2:1 hydrous clay intermediate* content. Tanada (54) reported that some of the highly weathered soils in Hawaii contained significant quantities of potassium. The result from this investigation shows that the potassium is high in the clay fractions of the A horizons.

Aluminum is very low in the coarse and medium silt fractions of the A horizons, and increases with decreasing size. The C and D horizons both showed high aluminum content. In all cases in which iron increases, aluminum shows a proportionate decrease. This can be observed from the chemical data of the coarse and medium silt fractions.

Silica in the fractions analyzed for silica is approximately of equal concentration except in the D horizon. This is significant in considering soil development in the tropics. Silica is lower in the clay fractions of the C and D horizons (about 12%) than the silt fractions (20% or greater). Insufficient silica determinations were conducted to show the trend of silica distribution in the remaining horizons.

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* The hydrous clay intermediates include the 2:1 layer lattice minerals containing less potassium than illite and no basal 10 A spacing. This series of minerals was earlier termed "mica intermediates".

MINERAL CONTENT OF THE PROFILE

The mineral content of the profile and the distribution of minerals in different size fractions is presented in this section. The importance of the several types of data in estimating mineral content is nicely brought out in these analyses.

Mineral content of the various fractions.--The mineralogical content of the various size fractions of the Naiwa profile has been quantitatively estimated and results presented in Table 5. The data from the elemental analysis which was reported in the previous section were taken into account in the estimation.

Hematite is the dominant mineral in the A horizons. Although hematite appears to be concentrated in the A_2 horizon, the probable introduction of erosional material in the A_1 is suspected.

Titanium is also high in the A horizons. It is highly significant to note that titanium bearing minerals equivalent to 1 to 3 per cent TiO_2 were found to occur in smaller size fractions. However, TiO_2 is concentrated up to 10 to 17 per cent TiO_2 in the coarser fractions and surface horizons. This would indicate that titanium is resistant to weathering, since it accumulates in the more highly weathered surface horizons--depth function (32). The occurrence of TiO_2 in the coarser fractions in higher concentrations than in the finer fractions may indicate crystal growth. The diffraction line of 3.51 A for anatase was found in the coarse silt fractions of the A horizons. Figure 7a is marked "An" at the 3.51 A position of anatase. Association of titanium content with iron content suggests the presence of a titanium-iron mineral. However, ilmenite ($TiO_2 \cdot FeO$) lines could not be identified. Figure 7b is marked "I" at the

diffraction position where ilmenite lines would appear if present.

Gibbsite predominates in the B, C, and D horizons but is low in amounts in the surface horizons. On the other hand, quartz is low in the C and D horizons and increases with proximity to the surface.

Kaolinite is present both on the surface horizons and in the C and D horizons. The absence of kaolinite in the B horizon does not necessarily mean that the surface kaolinite is of foreign origin. At present too little is known of clay mineral formation, and therefore exact conditions for kaolinite formation is not known. In all the horizons there is a high content of amorphous silicate. At this time it could be just as probable that the surface condition favors crystal formation.

Previous work on the latosols of Hawaii gave little evidence for the presence of 2:1 layer-lattice silicates (37). In the less than 0.2 micron fraction of the A_1 and A_2 horizons, the hydrous clay intermediates were definitely identified. The powder patterns showed a general haze in the region of the 10-14 A lines. This phenomenon is often times attributed to halide absorption of the diffraction film; the evidence for 2:1 layer-lattice minerals being greater darkening of the pattern. The direct reading X-ray technique eliminated this problem (below). Also, it usually happens that hydrous clay intermediates occur with illite, which shows a rather sharp line at 10 A when present. Using the 10 A line of illite as a reference line, the darkening of the adjacent region is studied for the hydrous clay intermediates, the potassium content serving as an index of the amount present. In this profile, the illite has weathered to the hydrous clay intermediates, thereby lacking a distinct line at the 10 A position.

The samples were prepared employing the layer-lattice orientation technique and X-rayed using the XRD-3 apparatus. The 10-14 A line appeared

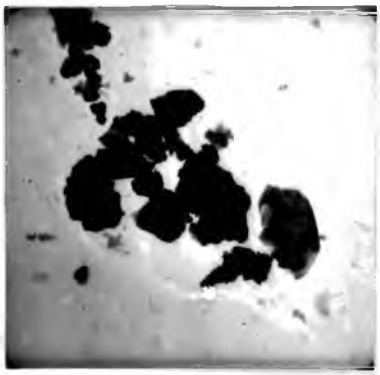


Figure 5.—Coarse clay fraction from the A_2 horizon. (6000X)

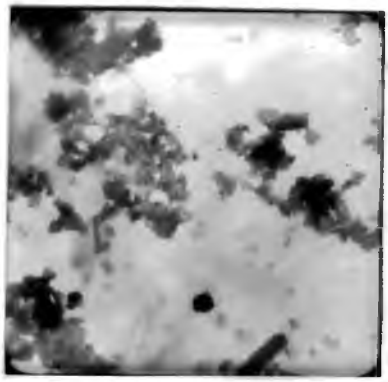


Figure 6.—Medium and fine clay fraction of A_2. Fine plates are characteristic of 2:1 layer silicates. (12,000X)

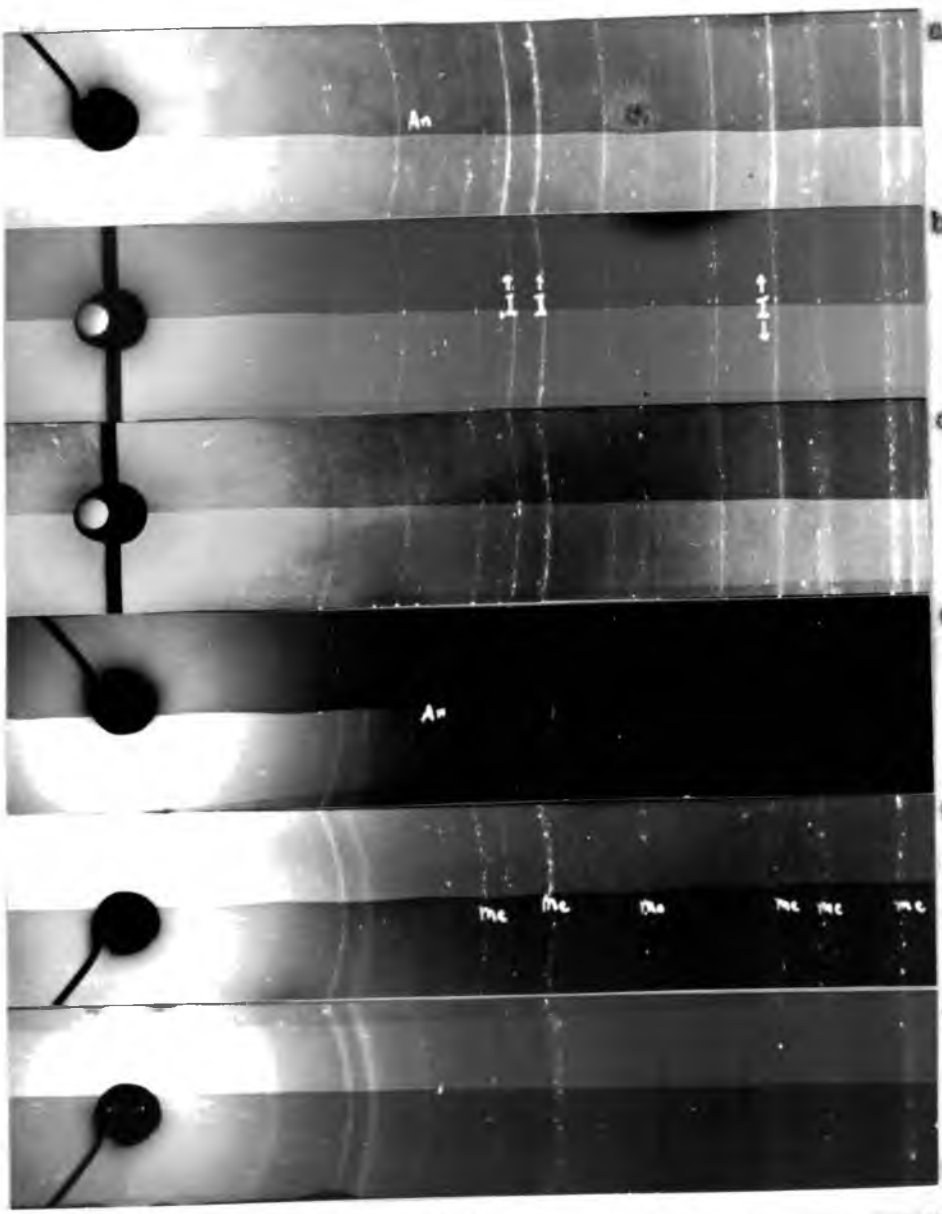
distinctly and the hydrous clay intermediates present up to 35 per cent in the medium and fine clay fraction of the A_1 horizon. The X-ray diffraction pattern is shown in figure 12. Electron micrographs indicated that 2:1 layer-lattice silicates could be present; figures 5 and 6 (above) are representative portions of the clay fractions from the A_2 horizon.

The high content of amorphous silicate is in accord with the findings of Kelley and Page (37). The results of this investigation modify their results to the extent that hydrous clay intermediates are identified. It is highly probable that the intensive weathering condition decomposes the layer silicates first formed, and insufficient time has elapsed for their removal by leaching.

Table 5. Mineralogical content of the Naiwa family of the Ferruginous Humic Latosol group.

Horison and depth, in cm		Mineral content in per cent*										
		Fl	Qr	Il	X	Mt	Kl	Gb	Ma	Gt	Hm	An	AS
Coarse silt, 50 to 20 microns													
A1	0-20	3	21	0	0	0	0	3	0	0	59	14	0
A2	20-35	0	9	0	0	0	0	4	0	0	74	17	0
A-B	35-50	0	5	0	0	0	0	16	0	0	66	13	0
B	50-100	0	5	0	0	0	0	20	0	0	47	8	20
C	100+	0	2	0	0	0	15	40	33	0	0	6	4
D	Partially dec. rock	0	0	0	0	0	35	35	17	0	0	3	10
Medium silt, 20 to 5 microns													
A1	0-20	16	20	0	0	0	0	11	0	0	46	7	0
A2	20-35	0	22	0	0	0	0	8	0	0	60	10	0
A-B	35-50	3	17	0	0	0	0	30	0	0	43	7	0
B	50-100	0	10	0	0	0	0	49	0	0	35	6	0
C	100+	0	2	0	0	0	20	55	10	0	0	1	12
D	Partially dec. rock	0	0	0	0	0	25	40	12	0	0	2	21
Fine silt, 5 to 2 microns													
A1	0-20	5	20	0	0	0	10	5	0	0	40	6	14
A2	20-35	0	20	0	0	0	0	15	0	0	52	9	4
A-B	35-50	0	17	0	0	0	0	30	0	12	25	5	11
B	50-100	0	17	0	0	0	0	40	0	13	15	4	11
C	100+	0	5	0	0	0	0	70	8	0	0	1	16
D	Partially dec. rock	0	5	0	0	0	5	65	5	0	0	1	19
Coarse clay, 2 to 0.2 microns													
A1	0-20	0	15	0	15	0	20	5	0	0	32	4	9
A2	20-35	0	12	0	5	0	10	10	0	10	35	6	12
A-B	35-50	0	17	0	0	0	0	15	0	10	35	6	17
B	50-100	0	15	0	0	0	0	25	0	13	35	6	6
C	100+	0	7	0	0	0	0	50	0	10	13	3	17
D	Partially dec. rock	0	3	0	0	0	0	60	5	0	0	1	31
Medium and fine clay, less than 0.2 microns													
A1	0-20	0	0	00	35	0	40	0	0	0	20	2	3
A2	20-35	0	0	0	20	0	20	10	0	8	15	3	24
A-B	35-50	0	5	0	5	0	5	30	0	9	20	3	23
B	50-100	0	5	0	0	0	0	50	0	14	25	3	3
C	100+	0	3	0	0	0	0	65	0	7	15	3	7
D	Partially dec. rock	0	3	0	0	0	0	75	6	0	0	1	15

* Fl = Feldspars; Qr = Quartz; Il = Illite; X = Hydrous clay intermediates; Mt = Montmorillonite; Kl = Kaolinite; Gb = Gibbsite; Ma = Magnetite; Gt = Goethite; Hm = Hematite; An = Anatase; AS = Amorphous silicates



a. XRD-3821
0-20 cm
A_1

b. XRD-3822
20-35 cm
A_2

c. XRD-3824
35-50 cm
A-B

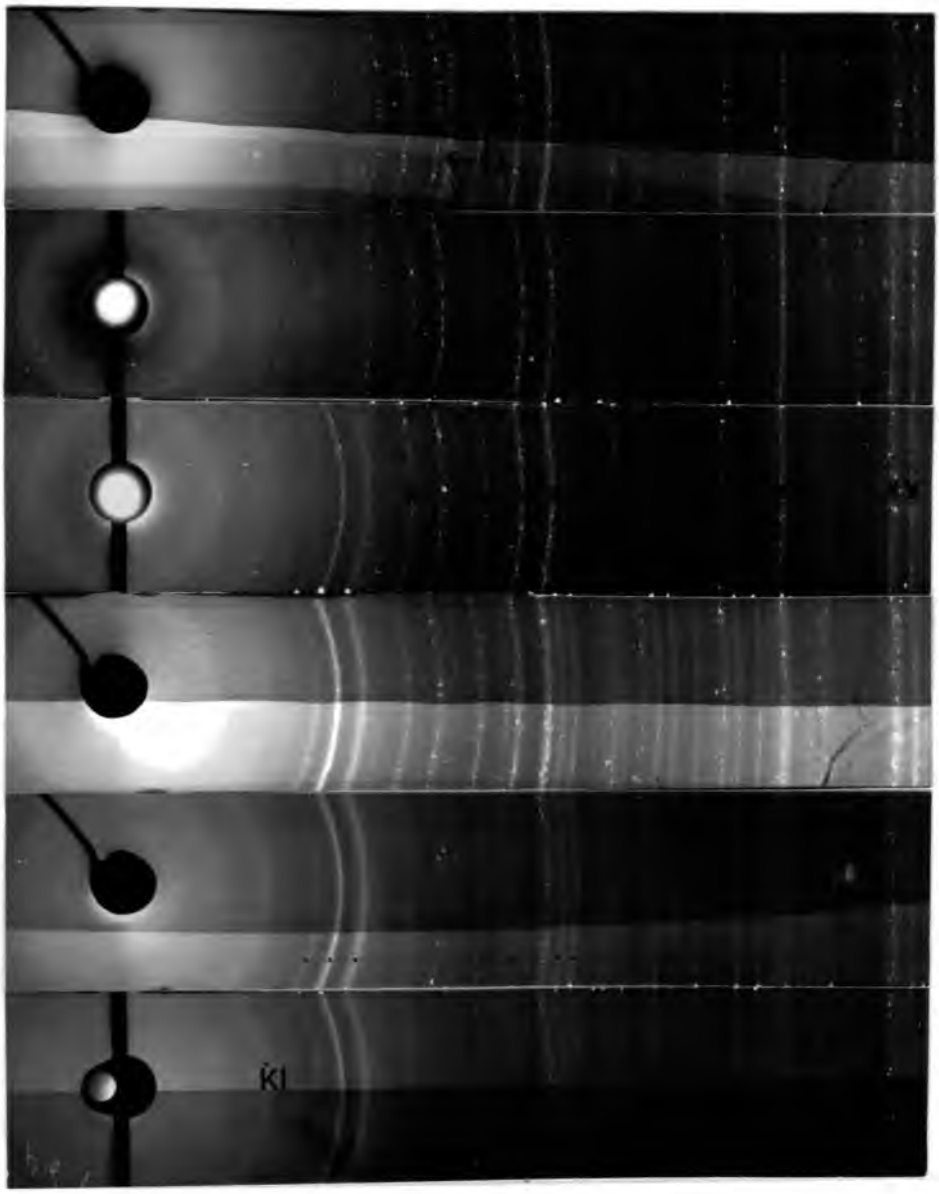
d. XRD-3825
50-100 cm
B

e. XRD-3823
100+
C

f. XRD-3963
Part. dec.
rock
D

Figure 7.--Coarse silt fraction of the Naiwa profile (50-20 microns).

me = Magnetite
I = Ilmenite
An = Anatase



a. XRD-3695
0-20 cm
A_1

b. XRD-3764
20-35 cm
A_2

c. XRD-3762
35-50 cm
A-B

d. XRD-3699
50-100 cm
B

e. XRD-3709
100+
C

f. XRD-3842
Part. dec.
rock
D

Figure 8.—Medium silt fraction of the Naiwa profile (20-5 microns).

X = Represents hematite lines

Kl = Kaolinite

Fl = Feldspars

. = Represents gibbsite lines

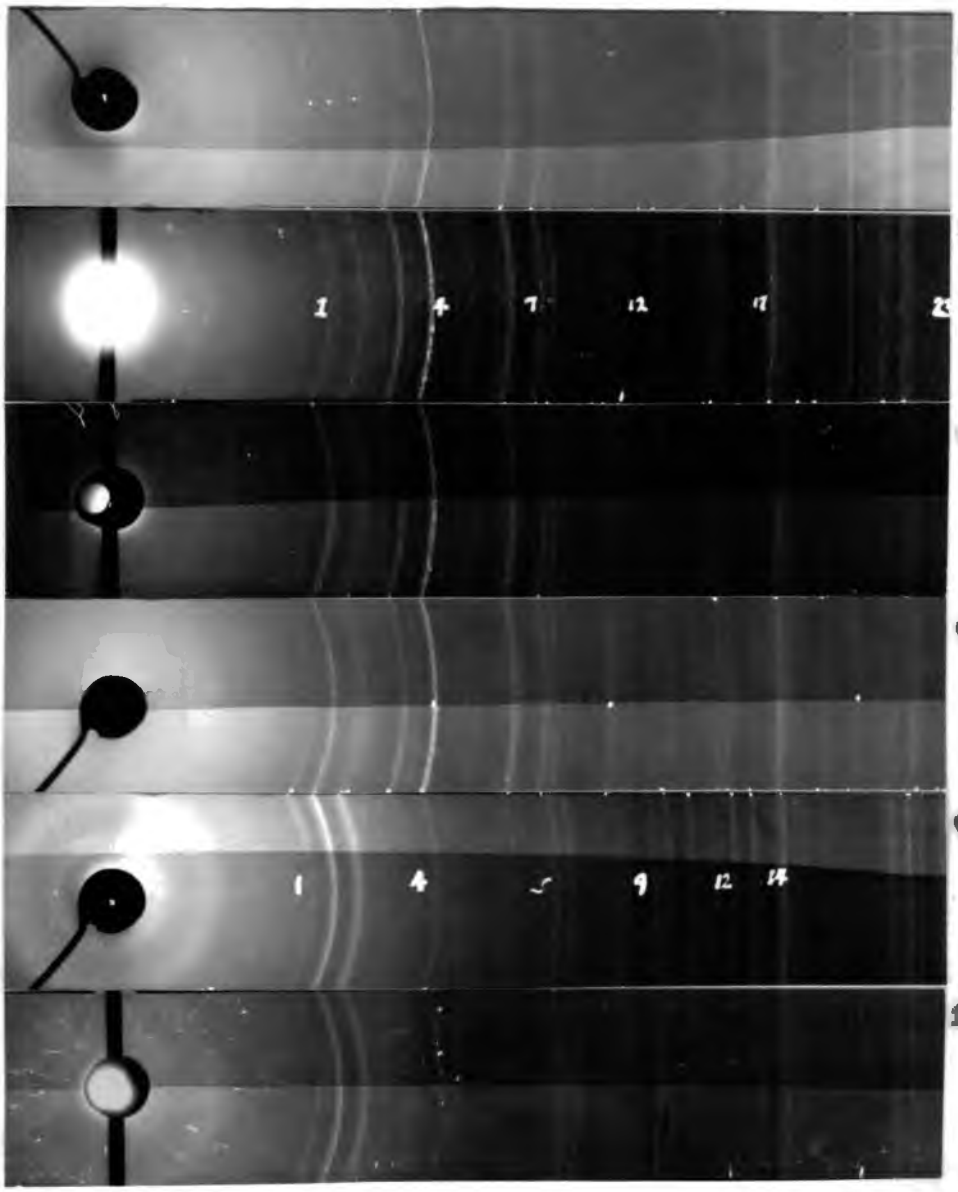


Figure 9.—Fine silt fraction of the Naiwa profile (5-2 microns).

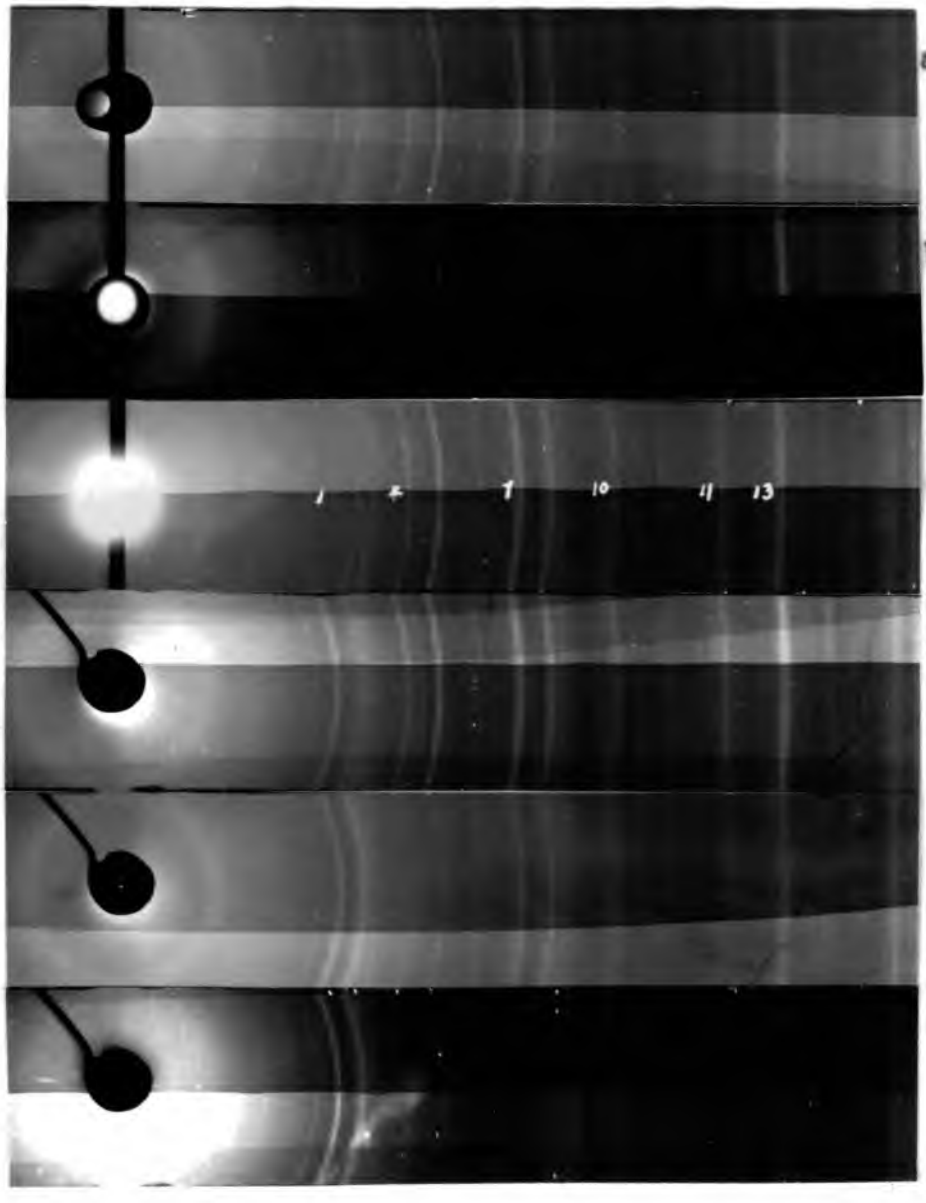


Figure 10.—Coarse clay fraction of the Naiwa profile (2-0.2 microns).

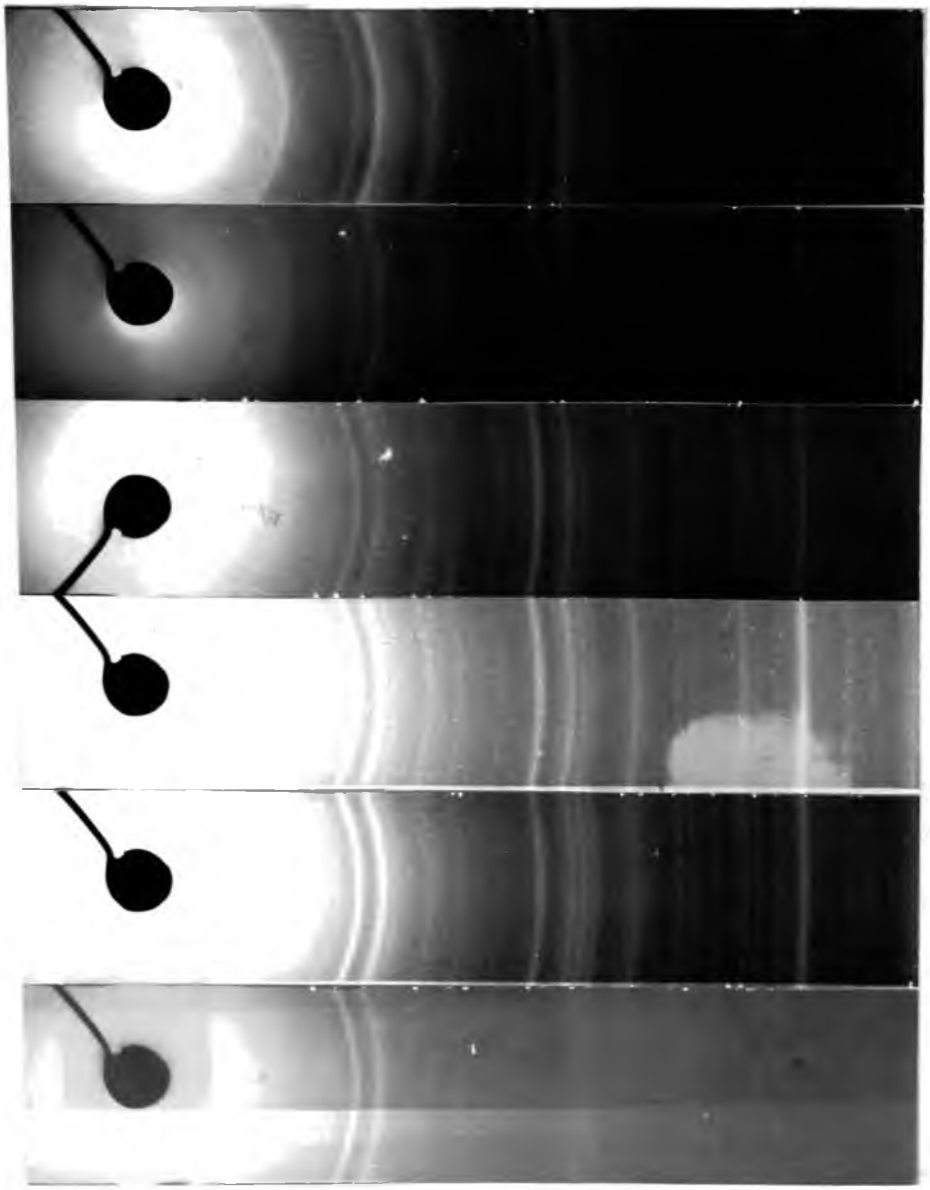
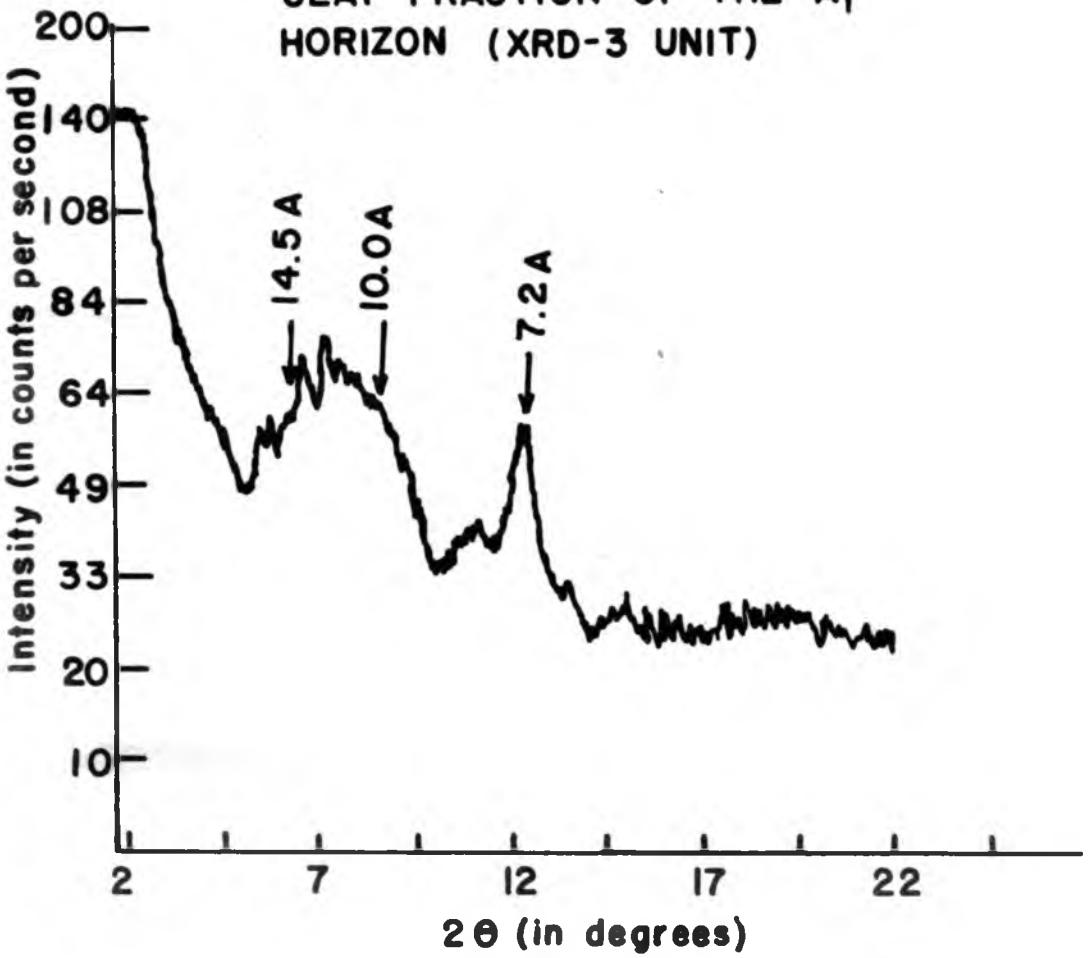


Figure 11.--Medium and fine clay fraction of the Naiwa profile (less than 0.2 microns).

FIGURE 12.-- X-RAY DIFFRACTION PATTERN FROM THE MEDIUM AND FINE CLAY FRACTION OF THE A_1 HORIZON (XRD-3 UNIT)



Mineral content as a function of particle size.--The results of this investigation again emphasize the necessity of size segregation for mineralogical identification and interpretation of the processes influencing soil formation. In latosolization, weathering of primary minerals into finer sized secondary minerals is accompanied by crystal regrowth of these secondary minerals to a large extent. Consequently although secondary minerals are primarily concentrated in the clay fractions for temperate region soils, latosols bring out the need to study larger size fractions up to the silt size range for correct interpretation of the weathering processes.

Hematite constitutes the major mineral in the silt fractions of the A_1 horizon. In the clay fractions, the layer-silicates predominate with kaolinite and hydrous clay intermediates being present. In the medium silt fraction of the A_1 horizon, feldspars are present. This fact necessitates consideration of possible source of erosional deposition before pedogenic processes are discussed.

The A_2 horizon showed an intense diffraction pattern of hematite in the coarse silt fraction, and chemical analysis revealed 74 per cent Fe_2O_3. It is significant to note that this fraction constitutes over 20 per cent of the A_2 horizon. In all cases where hematite is found in the coarser fractions, the diffraction lines of this mineral show a spotted character denoting large crystals rather than aggregates (see figure 8).

The A-B transition zone still contains high concentrations of hematite; however, gibbsite in this zone is much higher than the A horizons. There is no evidence for the presence of layer silicates except in the medium and fine clay fractions where very weak lines are present.

Gibbsite is dominant in the medium silt, fine silt, and medium and fine clay fractions of the B horizon. The highest content of goethite

and hematite of this horizon is in the coarse clay fraction. The fraction constitutes 30 per cent of the horizon (Table 3), the highest content of particles in this horizon.

In both the C and D horizons, gibbsite is present as the dominant mineral in all of the fractions. Although the iron mineral magnetite predominates in almost all cases, goethite and hematite are present in the finer fractions of the C horizon. In the larger size fractions, kaolinite is present in significant quantities. The D horizon contains more kaolinite than the C horizon.

In the finer size fractions appreciable amounts of unidentified alumino-silicates and silica are present. This conclusion was derived from X-ray and elemental analysis data. Although elemental determinations revealed appreciable concentrations of silica, only a faint quartz line was discernible in the medium and fine clay. The crystals of alumino-silicates may have been too small for X-ray diffraction, and electron diffraction may reveal information concerning sub-X-ray crystallinity.

WEATHERING STAGE OF THE NAIWA PROFILE

The following discussion of the weathering stage is developed in order to bring additional information to bear on the fundamental generalizations of the proposed weathering sequence (32).

Weathering stage as a function of profile depth.--The increase in weathering stage with proximity to the surface is exemplified by the distribution of the minerals in the profile. The high content of TiO_2 (Stage 13) and hematite (Stage 12) is in the A horizons, with increasing gibbsite (Stage 11) in the B, C, and D horizons, in accord with the horizon depth function (32). The weathering stage of the A_2, B, and C horizons (all fraction weighted for each horizon) is graphically presented in figure 13.

Table 6 gives the weight percentage of the minerals less than 50 microns occurring in this profile. The weathering mean is given in the last column. The mean was calculated in the following manner. The sum of the product of the percentage of each times its weathering stage was obtained. The sum was divided by the total percentage of minerals to give the mean value. Mathematically stated, it is:

$$\text{Weathering Mean} = \frac{\text{(percentage of mineral X weathering stage)}}{\text{(total mineral percentage)}}$$

The minerals used in the calculations were those which fell on the normal distribution curve. Quartz and hydrous clay intermediates were neglected in the calculations because of the uncertainty of their origin. If they are considered, the weathering mean decreases as a consequence of their position in the weathering stage; and the weathering mean show a reversal of the depth function for the A horizons relative to deeper horizons.

FIGURE 13.-- WEATHERING STAGE OF THE NAIWA PROFILE

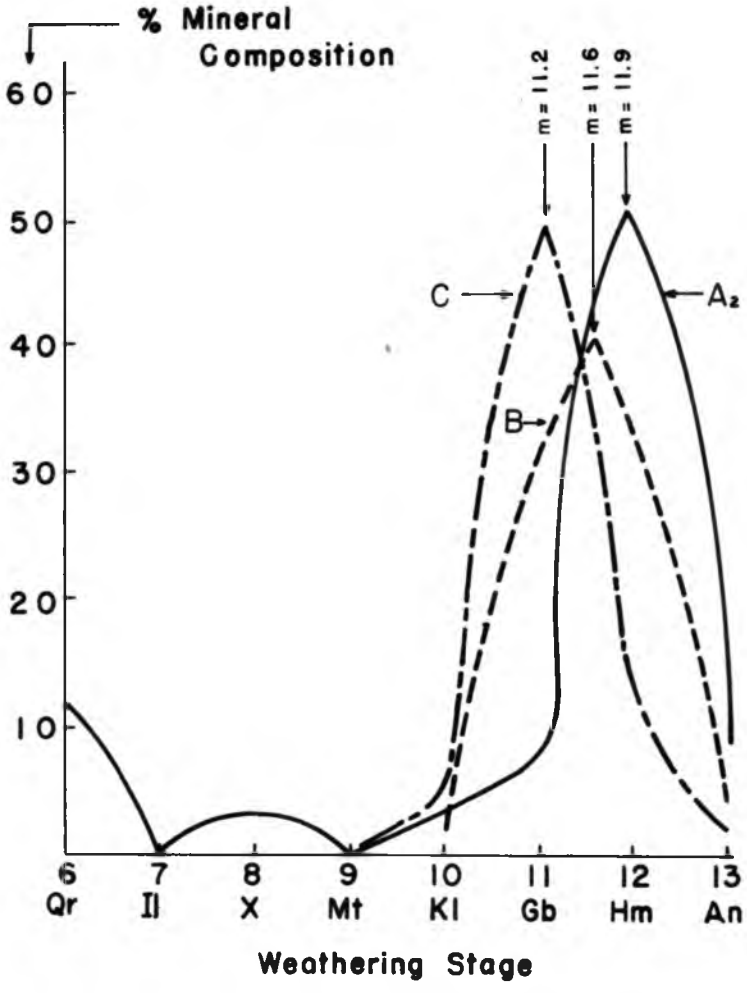


Table 6. Total mineral percentage and the calculated weathering mean of the horizons.

Horizon and depth, in cm		Mineral content in per cent*												
		Fl 5	Qr 6	Il 7	I 8	Mt 9	Kl 10	Gb 11	Ma 12	Gt 12	Hm 12	An 13	AS	Weathering mean
A_1	0-20	5	15	0	7	0	11	5	0	0	35	6	16	11.7
A_2	20-35	0	12	0	3	0	4	8	0	3	48	9	13	11.9
A-B	35-50	0	11	0	1	0	1	20	0	7	27	5	28	11.7
B	50-100	0	9	0	0	0	0	31	0	9	25	4	22	11.6
C	100+	0	3	0	0	0	5	48	6	3	5	2	28	11.2
D	Part. dec. rock	0	1	0	0	0	13	37	8	0	0	1	40	11.0

* Fl = Feldspars; Qr = Quartz; Il = Illite; I = Hydrous clay intermediates; Mt = Montmorillonite; Kl = Kaolinite; Gb = Gibbsite; Ma = Magnetite; Gt = Goethite; Hm = Hematite; An = Anatase; AS = Amorphous silicate. The numbers refer to the weathering stage according to Jackson, et al. (32).

In the development of the weathering stage, Jackson, et al. (32) considered minerals less than 5 microns. It has been established that secondary hematite crystals were large and concentrated in the coarse silt fractions in the A horizons, and they must be considered in the weathering stage. On the other hand, quartz may be either primary or secondary. Its absence in the finer size particles is evidence of its weatherability; but if it is secondary, then quartz must have a dual position in the weathering sequence. The latter position being in the vicinity of gibbsite and hematite. Quartz in coarse silt and sand sizes of particles is known to be one of the most resistant of all minerals to weathering. Until further information can be obtained concerning quartz, it is believed that the mean calculated without considering it in the coarser sizes is a better representation of the weathering stage of the profile. The frequency distribution curves shift to the right with proximity to the surface in the profile. The depth function states, "The weathering stage of the colloid of a soil horizon or of a sediment tends to advance with increasing proximity to the surface." (32, p. 1249). The statement for a soil colloid evidently is applicable for the entire silt and clay fractions when all or most of the minerals have weathered. The term "colloid" can be translated to "product of chemical weathering" for this latosol profile.

The normal shape of the frequency distribution curves is a striking corroboration of the proper order of listing of the different weathering stages, since improper order of listing would result in bimodal curves.

The absence of montmorillonite (Stage 9) in the A horizons can be explained by its relative ease of decomposition according to the normal weathering sequence. Montmorillonite has magnesium substituted in the

octohedral layer; the leaching out of magnesium in the horizon would prevent the formation of montmorillonite and cause the absence of stage 9. Similarly, the illite stage is largely past under intensive weathering which had been present is largely converted to the hydrous clay intermediates in the normal course of weathering.

Kaolinite-gibbsite sequence.—Some lines of investigation suggest that formation of gibbsite (Stage 11) might take precedence over kaolinite (Stage 10) in the weathering sequence and that their stage positions should be interchanged. Harrison (19) has concluded from his studies that under tropical conditions, the katamorphism of basic and intermediate rocks is accompanied by the formation of aluminum hydroxide or gibbsite, which is succeeded by resilication. Alexander, et al. (1) have investigated several rocks and soil and concluded that the primary weathering products in soils of southeastern United States contained gibbsite from norite, amphibolites, an epidote greenstone schist, a diabase, and muscovite-biotite schist. Goldman and Tracey (13) have stated that in the Arkansas deposits, bauxite is formed directly from nepheline syenite rather than kaolinized nepheline syenite and that the gibbsite may be resilicated by silica solutions penetrating the deposit from more recent over-burden.

These examples may be explained on the basis of rapid traverse of the sequence from primary rock to stage 11 (gibbsite) without much accumulation of intermediate products. The weathering would thus be largely a "binary weathering reaction" (32). Resilication to kaolinite in these cases, particularly of the Arkansas bauxite (13) came as a reversal of the weathering through enrichment of percolating solutions with silica.

It may be supposed that the silica component of soil solutions ordinarily effect the silication of alumina concurrent to its release by hydrolysis of primary aluminum silicates. In the cases cited, the silication did not occur or was followed by immediate desilication.

In soils of temperate zones, kaolinite appears in association with micas, vermiculite, and montmorillonite; hence its assignment to stage 10 (32). In the present investigation of a soil developed in a tropical zone, the D horizon was found to contain more kaolinite than the C horizon (as shown in the previous section), and that kaolinite decreased with proximity to the surface in accord with the depth function of the weathering sequence. It is probable that a very rapid decomposition of kaolinite occurs and the gibbsite grows to large size crystals.

Gibbsite-hematite sequence.—Placing hematite at a higher stage (Stage 12) than gibbsite (Stage 11) may not at first seem valid, since gibbsite accumulates under continuously moist climate (55). This order is valid, however, according to the conditions considered to be positive, i.e. to greater degree of weathering. Oxidation is taken as the positive direction; whereas reduction is negative as a weathering process (highly weathered soils have good oxidation). Accumulation of hematite occurs under good oxidising conditions. Gibbsite on the other hand forms not only under oxidising conditions but also under water-logged conditions by decomposition of the silicates. When reducing conditions occur, ferric o ironis easily reduced to ferrous, which is soluble, and iron will be leached while aluminum hydroxide will accumulate under reducing conditions. Also gibbsite occurs so readily as to have been considered possibly to precede kaolinite in the sequence under some circumstances (previous section).

Sequence within the hematite stage.—The primary mineral magnetite is placed in stage 12 by virtue of its relative stability to weathering (32).

The presence of goethite in the finer sized fractions suggests that hematite precedes goethite in the sequence according to the particle size function. However, the minerals of stages 10, 11, and 12 exhibit a great tendency to undergo crystal regrowth and occur independently of particle size (32, p. 1248). Investigations of a latosol profile from the Dominican Republic* showed that goethite decreased with decreasing size and hematite increased with decreasing size. The latter profile is less weathered than the profile from Hawaii; consequently the sequence of weathering is magnetite (primary mineral)---goethite---hematite.

* From X-ray diffraction data obtained in Soils 221 laboratory by J. C. Kaudy, Soils Department, University of Wisconsin.

GENESIS OF THE NAIWA FAMILY OF THE FERRUGINOUS HUMIC LATOSOLS

The genesis of the latosols in Hawaii especially the Ferruginous Humic Latosol group has been discussed by several writers (12)(55)(56)(57). Previous writers have depended on elemental analyses and ratios, and field observations in postulating the pedogenic processes and transformations occurring in these soils. The following considerations have been made primarily on the basis of the mineralogical content from a representative latosol.

In this investigation, hematite has been found to be concentrated in the coarser fractions at the surface and A_2 horizons; and in the B horizon, both hematite and goethite are present. Hematite and goethite from the B horizon is concentrated in the finer size fractions. In the D horizon, no hematite or goethite could be identified, the iron oxide mineral being magnetite. The C horizon contained magnetite in the coarser fractions with hematite and goethite being present in the smaller size fractions. Thus it would seem that magnetite decomposed to give goethite, which in turn lost its hydroxyl and transformed to hematite. Under alternating moist and dry conditions, hematite crystals may grow into larger sizes, resist weathering and finally concentrate in the A horizons. Previous work has shown limonite to be present in appreciable quantities(58). The diffraction pattern of limonite is identical* to goethite except that the particle-size is smaller. A portion may be amorphous so that its detection would be impossible by X-ray diffraction.

Sherman (56) however maintains that upward movement of capillary water containing dissolved iron and titanium is responsible for the

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* Observed in this laboratory by Dr. M. L. Jackson.

formation of the ferruginous crust. This contention is substantiated by the identification of anatase associated with hematite in the A horizons. The presence of TiO_2 as anatase indicates it is a product of weathering. The TiO_2 in the medium and fine clay fractions shows the resistance of titanium minerals to solution and leaching. Accumulation of TiO_2 and Fe_2O_3 in the surface horizons is in accord with the theory of Fujimoto and Sherman (12) of the upward movement of water containing soluble and colloidal TiO_2 and Fe_2O_3 and eventual deposition and accumulation in the A_2 horizon. The "upward" movement includes lateral movement to the surface of lower-lying soils (56).

The high content of silica in the A_1 horizon may be explained by the presence of feldspars, layer-silicates, and quartz. In nearly all particle-sizes of this profile, quartz is highest in this horizon. The mineralogical content of the A_1 horizon presents an interesting problem in interpreting the pedogenic process which this soil has undergone. The mineralogical content of the A_1 horizon is summarized below from Table 5, page 31.

Stage	Mineral	Percentage in fraction 20-50	5-20	2-5	0.2-2	0.2
	Amorphous silicate	0	0	14	9	3
5	Feldspars	3	16	5	0	0
6	Quartz	21	20	15	15	0
8	Hydrous clay intermediates	0	0	0	15	35
10	Kaolinite	0	0	10	20	40
11	Gibbsite	3	11	5	5	0
12	Hematite	59	46	40	32	20
13	Anatase	14	7	6	4	2

The mineralogical content is different from the A_2 horizon immediately below; the question arises as to whether the A_1 horizon is of the same origin as the remaining horizons or whether erosional deposition has played a major role in the formation of this horizon. It should be

reiterated that careful consideration was given the A_1 horizon of similar profiles occurring on different islands; and in every case an A_1 horizon was present; in some cases the A_1 had eroded away, but positive evidence of its former existence was found. The A_1 horizon was found to exist even where there was very little or no evidence of later deposition.

On the basis of the development of the profile from the same parent material, the genesis of the profile may be as reported by Sherman (56), and a portion of his publication is quoted below.

> "As the soil matured the internal drainage became poor due to the development of impervious clay layers. With the development of the poor internal drainage more of the percolating water will move down the slope laterally and less will percolate through the soil and its weathered parent material. When the lateral movement of percolating water reaches areas having an alternating wet and dry season, conditions become favorable for the capillary rise of the percolating waters during the dry season. The capillary rise of the percolating waters to the surface is greatly enhanced by the benches of level areas of the slopes. A similar case of enrichment of soils of lower elevations by lateral movement of percolating waters has been proposed by Green.
>
> The dissolved iron and titanium are brought to the surface in the capillary water. The iron is stabilized by its oxidation to the ferric form. During the dry season the iron oxide which probably exists as goethite and the hydrated titanium oxides are dehydrated to form the minerals hematite and anatase, respectively. The dissolved silica in the percolating waters would probably rise to the very surface before dehydration. The data in Table 1 would support this hypothesis."

Although the data from his table is not the same as the data from this investigation, both profiles belong to the Naiwa family of the Ferruginous Humic Latosol group. Geologic evidence shows that Sherman's profile from the Island of Kauai is older than that from this investigation which came from the Island of Maui. Nevertheless both profiles show high silica content in the A_1 horizon. The silica from the profile from Maui is in the form of quartz, kaolinite, hydrous clay intermediates and

feldspars. The absence of kaolinite and hydrous clay intermediates in the B horizon indicates that these minerals were formed later in the process of soil formation. The dissolved silica may combine, on coming to the surface, with gibbsite to form kaolinite and hydrous clay intermediates. The formation of kaolinite from gibbsite has been discussed by Goldman and Tracey (13). As more of the gibbsite is combined with silica, the source of gibbsite is depleted and the remaining silica probably forms quartz under the alternating moist and dry climatic conditions. It has been shown that crystal formation begins with microaggregates with later "filling in" of the open spaces to form larger crystals (5), and it has also been shown that similar minerals tend to come together to form aggregates (39); consequently it would not be unreasonable to suppose that X-amorphous silica grow into quartz under alternating wet and dry conditions. The high content of unidentified silica or silicate in the finer fractions of the lower horizons further lend support to the possiblity of upward movement of silica.

However the feldspar content in the medium clay fraction cannot be disregarded. It should be mentioned that the 16 per cent reported in Table 5 is the maximum content possible by the sodium and potassium analyses. A careful study of the history and topographic features of this area may elucidate the status of the A_1 horizon. If the A_1 is of different parent material, the formation of kaolinite and hydrous clay intermediates may be from the weathering product of the feldspar. The source of potassium in the A_1 horizon may be from the decomposed organic matter and the potash feldspar. In any case the lateral movement of water is not to be disregarded, and the upward movement of the capillary water may be partly the source of potassium. Tanada (58) found potassium to be

rather high in some of the more highly weathered soil colloids, the identification of hydrous clay intermediates explains the manner of retention of potassium.

It should be emphasized that further work will be conducted along this line with soils of the Ferruginous Humic Latosol group from other locations. Samples from different locations may help to explain the A_1 horizon.

The mineralogical content of the C and D horizons show that kaolinite is undergoing rapid decomposition. Unlike the kaolinite in the surface horizons, that in the C and D horizons is concentrated in the silt size fractions. The silica in the finer fractions may be due to the destruction of kaolinite in the course of weathering.

SUMMARY

A representative profile from the Naiwa family of the Ferruginous Humic Latosol group was size-segregated, chemically analysed for iron, titanium, potassium, aluminum, and silicon, and X-rayed. The sodium-saturation and alkalinity of pH 9.5 with NaOH were found to be only a moderately satisfactory dispersion method for the mineralogical analysis; preliminary investigations showed that boiling in 2 per cent Na_2CO_3 solution was a more effective dispersion treatment. The X-ray diffraction procedure employed for temperate region soils was found to be applicable to this profile.

The results of this investigation may be summarized as follows:

1. Size-distribution analysis revealed the A_1, A_2, and C horizons to be silty clay loams, the D horizon to be silt loam, and both the A-B transition and B horizons to be clays in textural class.

2. The minerals found to be present in this profile are hematite, goethite, gibbsite, anatase, quartz, kaolinite, hydrous clay intermediates, magnetite, and feldspars.

3. Hematite was found to be highest in the A_2 horizon (51%). The highest content of hematite in any one size fraction is in the 20-50 micron fraction of the A_2 horizon. This fraction contained over 70 per cent hematite and made up 21 per cent of the horizon. The hematite particles of these coarse fractions was identified as single crystals rather than aggregates.

4. Goethite was found in the finer size fractions of the A-B, B, and C horizons, being present in quantities of 7 to 14 per cent in each fraction in which it was identified.

5. In the D horizon, no hematite was identified, the iron oxide mineral being magnetite.

6. Quartz is highest in the A_1 horizon making up 15 per cent of the horizon and decreasing with increasing depth.

7. Gibbsite is highest in the C and D horizons. It comprises 48 per cent and 37 per cent respectively. The lowest content is in the A_1 horizon (5%).

8. Kaolinite in the A horizons was found to be concentrated chiefly in the fine silt and clay size fractions; 11 per cent, 4 per cent, and 1 per cent respectively in the A_1, A_2, and A-B horizons. In the C and D horizons, kaolinite was identified in the silt size fractions; 13 per cent in the D horizon and 5 per cent in the C horizon.

9. Feldspars were identified in the A horizons. Only the A_1 horizon contained significant quantity, making up 5 per cent of the horizon.

10. The highest TiO_2 content is in the A_2 horizon. Anatase was identified on the basis of the 3.51 A line. TiO_2 and Fe_2O_3 content show a direct relationship as to amount.

11. The clay-size fractions showed a high content of X-amorphous alumino-silicates and silica; the highest content being in the 2-0.2 microns fraction of the D horizon (31%).

12. The weathering stage of the various horizons has been calculated. The highest stage is the A_2 horizon (Stage 11.9) and the lowest is the D horizon (11.0). The position of the distribution curves is in accord with the depth function of the weathering sequence previously reported.

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